New Heteroaromatic Compounds. XXXII.[1] Properties of 10,9-Borazaronaphthalene and 9-Aza-10-boradecalin[2]

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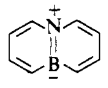
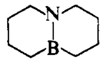
Abstract: The ^{11}B nmr spectra, and mass spectra, of 10,9-borazaronaphthalene (I) and 9-aza-10-boradecalin (II) have been measured; the results are consistent with current views concerning the aromaticity of I. The photoelectron spectra of I, II, and naphthalene (III) have also been measured; comparison of the spectra of I and III indicated a close similarity in electronic structure.

Recently we described[5] the preparation and properties of 10,9-borazaronaphthalene (I), a compound which should, according to our earlier studies,[6] be aromatic since it is isoelectronic with naphthalene (III). Indeed, the method of preparation, *i.e.*, dehydrogenation of 9-aza-10-boradecalin (II) indicated that I must be aromatic, and it was shown that its proton nmr spectrum[5,7] and chemical properties[5] were consistent with such a formulation. Here we report some additional measurements for this novel and interesting heteroaromatic system.



I



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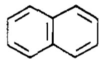
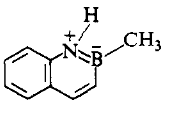


III

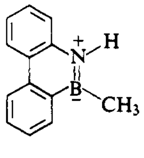
^{11}B Nmr Spectra

In a previous communication[8] it was suggested that ^{11}B nmr spectroscopy can be used as a criterion of aromaticity in boron-containing heterocycles, the boron atoms in compounds such as 2-methyl-2,1-borazaronaphthalene (IV) or 10-methyl-10,9-borazarophenanthrene (V) showing upfield shifts which were attributed to magnetic shielding either by aromatic ring currents or by increased π-electron density on boron due to the aromaticity of the boron-containing ring. These arguments were, however, weakened by the lack of suitable nonaromatic reference compounds for comparison. In the case of I, the decalin analog II clearly provides such a criterion; we have therefore measured the ^{11}B nmr spectra of I, II, and of the hydrate (VI)[5] of II, using the techniques described earlier;[8] the results are shown in Table I, together with some related values for comparison.

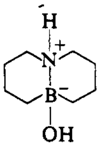
The large upfield shift on passing from the decalin analog (II) to the naphthalene analog (I) clearly parallels those reported for other similar compounds,[8] and may very well be due, at least partly, to aromaticity in I.



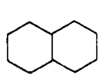
IV



V



VI



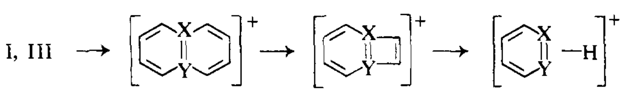
VII

However the results in the literature for vinylboron derivatives (Table I) suggest that the difference may in fact be due to local interactions, depending on the hybridization of the carbon atoms adjacent to boron; thus the difference in chemical shift between trimethylboron and methyldivinylboron (22.0 ppm) is in fact greater than that between I and II. The large difference between II and VI (42 ppm) can, on the other hand, be attributed with some certainty to the change in hybridization of boron, the chemical shift for VI being similar to those of analogous ions of the type R_3B^-OH.[9]

Mass Spectra

Figure 1 shows the mass spectra of I and II, together with those of III and decalin (VII) for comparison; it is immediately apparent that the spectra of the boron-containing compounds are very similar to those of their hydrocarbon analogs.

Thus by far the most intense peaks in the spectra of I and II are those corresponding to the molecular ions, and the fragmentation patterns are similar, *viz.*[10]



I, *m/e* 129 (100)	103 (12)	76 (21)
III, *m/e* 128 (100)	102 (7)	75 (6)

This suggests strongly that I, like III, is aromatic. The only real difference between the two spectra is that I gives larger yields of fragmentation products; this again would be expected, since I must undoubtedly be less aromatic than III.

In the case of II, the most intense peak is that corresponding to the ion $(II\text{-}H)^+$; this of course would be expected, since II is not aromatic, and so, like amines,

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(1) Part XXXI: M. J. S. Dewar and R. Jones, *Tetrahedron Letters*, 2707 (1968).

(2) This work was supported by grants from the Air Force Office of Scientific Research (Grant No. AF-AFOSR-1050-67) and from the Robert A. Welch Foundation.

(3) Robert A. Welch Postdoctoral Fellow.

(4) Robert A. Welch Postdoctoral Fellow.

(5) M. J. S. Dewar and R. Jones, *J. Am. Chem. Soc.*, **90**, 2137 (1968).

(6) See M. J. S. Dewar, *Progr. Boron Chem.*, **1**, 235 (1964); "Boron–Nitrogen Chemistry," K. Niedenzu, Ed., Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 227.

(7) M. J. S. Dewar, G. J. Gleicher, and B. P. Robinson, *J. Am. Chem. Soc.*, **86**, 5098 (1964).

(8) F. A. Davis, M. J. S. Dewar, and R. Jones, *ibid.*, 90, 706 (1968).

(9) M. J. S. Dewar and R. Jones, *ibid.*, **89**, 2408 (1967).

(10) Abundance of ions in the mass spectra are indicated in parentheses, relative to the base peak as 100.

Table I. ^{11}B nmr Spectra of I, II, and VI

Compound	Solvent	Chemical shift[a]	Line width[b]
II	Chloroform	-42.9 ± 0.5	111
I	*n*-Hexane	-28.4 ± 0.5	85
VI	Acetone	-1.0 ± 0.5	80
$B(CH_3)_3$		-86.4[c]	
$CH_2{=}CHB(CH_3)_2$		-74.5[d]	
$(CH_2{=}CH{-})_2BCH_3$		-64.4[d]	
$(CH_2{=}CH{-})_3B$		-55.2[d]	

[a] In parts per million (ppm), relative to boron trifluoride etherate (BTE). [b] In hertz (Hz), at half-height. [c] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). [d] C. D. Good and D. M. Ritter, *ibid.*, **84**, 1162 (1962).

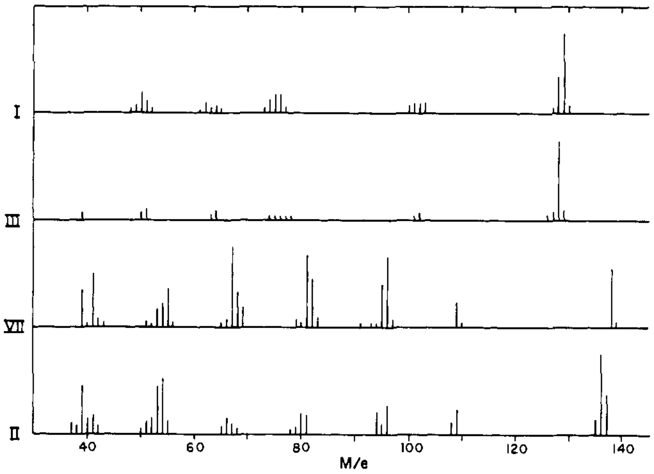
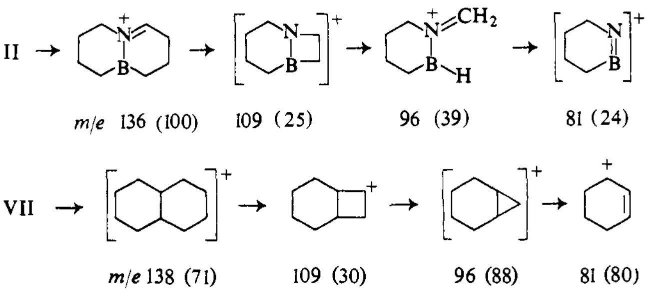


Figure 1. Mass spectra of I, II, III, and VII.

should easily lose a hydride ion from a position adjacent to nitrogen to give a methyleneammonium ion. In VII, where the tendency to lose H^- is much less marked, the peak for the molecular ion VII^+ is more intense than that for $(VII\text{-}H)^+$. Apart from such minor differences, however, the spectra are very similar, the mass peaks indicating analogous fragmentation patterns, *viz.*



Photoelectron Spectra. Ionization Potentials

We have estimated the ionization potentials of I, II, and III from their photoelectron spectra. The recently developed technique of photoelectron spectroscopy[11] is an extremely valuable method for determining ionization potentials in that it not only gives values for adiabatic first ionization energies but also ionization energies corresponding to the removal of electrons from inner molecular shells.

Our photoelectron spectrometer is similar to that described by Al-Joboury and Turner[11a] in that it contains a retarding potential kinetic energy analyzer; a complete description of the instrument has appeared elsewhere.[12] Typical representations of the photoelectron spectra of naphthalene (III), 10,9-borazaronaphthalene (I), and 9-aza-10-boradecaline (II) appear in Figure 2. Although the photoelectron output current was differentiated, the spectra resemble photoionization step curves because electrons traveling in paths other than parallel to the retarding potential field cause low kinetic energy "tails" on the peaks; the initiation of the peaks or the "breaks" in the photoelectron spectra correspond to adiabatic ionization potentials, agreeing with those derived from the convergence limits of Rydberg series. All samples were subjected to several cycles of freezing and evacuation on a high-speed vacuum line, and sublimation, before evaporation into the ionization chamber.

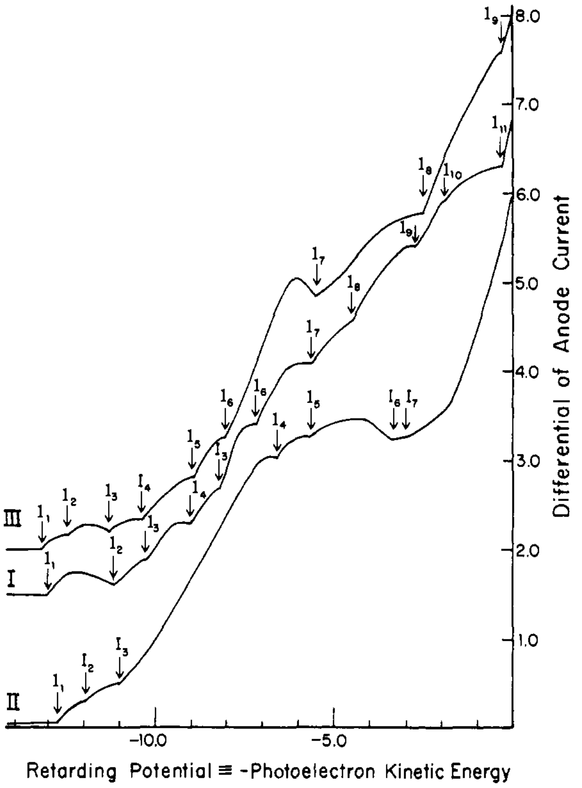


Figure 2. Photoelectron spectra of I, II, and III at pressures of 0.027, 0.026, and 0.032 mm, respectively.

The ionization potentials corresponding to prominent breaks in the photoelectron spectra of I, II, and III are

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(11) (a) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 5141 (1963); (b) M. I. Al-Joboury and D. W. Turner, *ibid.*, 4434 (1964).

(12) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

Table II. Ionization Potentials from Photoelectron Spectra

Compd	I,[a] eV	Higher ionization potentials, eV
I	8.24	10.07, 10.95, 12.23, 13.07, 14.05, 15.53, 16.74, (18.43), (19.35), (21.01)
II	8.47	(9.28), 10.22, 14.60, (15.53), (17.84), (18.23)
III	8.11	8.79, 9.96, 10.90, 12.26, 13.22, 15.73, (18.65), (21.03)
cis-VII	9.40	(10.93), 13.68, (18.30)
trans-VII	9.35	10.67, 13.84, 15.21, (17.89)

[a] First ionization potential.

listed in Table II. Values in parentheses are regarded as uncertain, because the breaks were either not completely reproducible or not as sharp as the others. Nevertheless the standard deviations for the independent determinations of these uncertain values never exceeded 0.07 eV and were mostly in the range 0.03–0.05 eV. Values are also listed for *cis*- and *trans*-decalin (VII).[12]

The first ionization potential of II (8.47 eV) is much less than that of VII; the first ionization of II must therefore correspond to loss of a nitrogen lone-pair electron. The value for II is significantly higher than those of typical tertiary amines (Me_3N, 8.12 eV;[11b] Et_3N, 7.84 eV[11b]); since the BN σ bond is much more polar in the sense B^+–N^- than is a CN σ bond, and since negative charge on nitrogen should reduce the ionization potential of its lone-pair electrons, the high ionization potential of II must indicate relatively strong π bonding. Simple-minded MO theory would require the change in ionization potential to be about one-half the π-bond energy; the value in Table II (8.47 eV) would then imply a bond energy of *ca.* 20 kcal/mol for the BN π bond. The strength of this bond can be estimated from the barriers to rotation about the BN bond in aminoboranes of the type R_2BNR_2; those that have been measured are indeed of this order of magnitude.[13]

In a previous paper[12] we showed that ionization potentials measured by photoelectron spectroscopy correlate extraordinarily well with orbital energies calculated by the MINDO SCF MO method.[14] On this basis, the first five ionizations of naphthalene were attributed to ionizations from π MO's, the weaker σ ionizations not being resolved by our spectrometer. This assignment was supported by a second semiempirical SCF MO treatment of naphthalene,[15] based on the Hückel σ,π approximation; the energies and eigenvectors of the MO's given by this π approximation agreed extraordinarily well with those given[16] by an earlier SCF approximation (PNDO)[17] in which all the valence shell electrons are taken into account, and also with later MINDO calculations.[14]

As yet no calculations are available for compounds containing boron; however the results in Table II, together with the SCF MO calculations, seem to suggest very strongly the following assignment of the first five ionizations of I to π MO's.

The MO's of naphthalene are of course either symmetric, or antisymmetric, to reflections in a plane passing through the 9,10-carbon atoms and perpendicular to the molecule; antisymmetric MO's therefore have a node passing through the 9,10 positions and AO's of those atoms do not therefore contribute to them. The energies of such MO's should therefore be little affected by changes in the 9,10 atoms; in particular, such MO's should survive unchanged if their atoms are replaced by boron and nitrogen, *i.e.*, they should survive more or less unchanged, and with unchanged energies, in I. Now the two antisymmetric π MO's in III correspond[14] to the ionization potentials at 8.11 and 10.90 eV; there seems little doubt that the ionization potentials at 8.24 and 10.95 eV in I must represent ionization from the corresponding antisymmetric π MO's.

In the case of naphthalene, the symmetric MO's have of course equal densities at the 9 and 10 positions; in I, however, they will tend to be concentrated more on nitrogen since nitrogen is so very much more electronegative than boron. This will lead to a change in the corresponding ionization potentials on passing from III to I which can be estimated approximately by using first-order perturbation theory.[18] If the coefficient of the 9 (or 10) AO in the corresponding MO ψ_μ of III is A_μ, and if the coefficient of the nitrogen and boron AO's in the corresponding MO ψ_μ' of I are $A_{N\mu}$ and $A_{B\mu}$, respectively, and if the coulomb integrals of nitrogen, carbon, and boron are respectively α_N, α_C, and α_B, then the difference in orbital energy (δE_μ) between III and I should be given approximately by

$$\delta E_\mu = A_{N\mu}^2\alpha_N + A_{B\mu}^2\alpha_B - 2A_\mu^2\alpha_C \qquad (1)$$

Owing to the polarization from boron to nitrogen in I

$$A_{N\mu}^2 > A_\mu^2 > A_{B\mu}^2 \qquad (2)$$

Also since nitrogen is more electronegative, and boron less electronegative, than carbon

$$\alpha_N + \alpha_B < 2\alpha_C \qquad (3)$$

From eq 1–3, δE_μ must be negative; the symmetric MO's in I should therefore have lower orbital energies than those in III and the corresponding ionization potentials of I should therefore be greater than those of III. On this basis it seems reasonable to correlate the ionization poten-

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(13) See, *e.g.*, H. Watanabe, T. Totari, K. Tori, and T. Nakogawa in "Nuclear Magnetic Resonance and Relaxation in Solids—Proceedings of the XIIIth Collogue Ampère," L. Van Garver, Ed., North-Holland Publishing Co., Amsterdam, 1965, p 374.

(14) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, in press.

(15) A. L.-H. Chung and M. J. S. Dewar, *ibid.*, **42**, 756 (1965); M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965); M. J. S. Dewar and C. deLlano, submitted for publication; C. deLlano Ph.D. Thesis, The University of Texas, 1968.

(16) N. C. Baird and M. J. S. Dewar, *Theoret. Chim. Acta*, **9**, 1 (1968).

(17) M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967).

(18) M. J. S. Dewar, *ibid.*, **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.

tials of I at 10.07, 12.23, and 13.07 eV, respectively, with those of III at 8.79, 9.96, and 12.26 eV.

According to this analysis, the ionization potential of I at 8.24 eV bears no relation to that of II at 8.47 eV. The former corresponds to ionization from an antisymmetric π MO concentrated entirely on carbon, the latter to ionization from a two-center π MO largely concentrated on nitrogen. In II, the nitrogen "lone pair" electrons occupy a single MO largely centered on nitrogen; in I, they are dispersed over the three symmetric π MO's.

We hope soon to establish suitable parameters for boron in our SCF MO treatments; it will be interesting to see if the calculated π-orbital energies in I agree with this interpretation of the photoelectron spectrum.

A New Mode of Decomposition of an Episulfone. Pyrolysis of the Episulfone of *cis*-Dibenzoylstilbene[1-3]

Donald C. Dittmer, George C. Levy, and George E. Kuhlmann

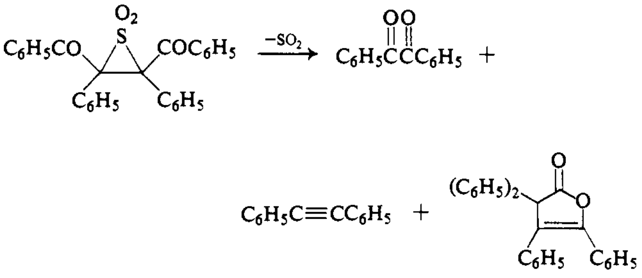
Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210. Received August 27, 1968

Abstract: Pyrolysis of the episulfone of *cis*-dibenzoylstilbene yields sulfur dioxide but unlike other episulfones does not yield the olefin but rather diphenylacetylene, benzil, and the lactone of 4-hydroxy-2,2,3,4-tetraphenyl-3-butenoic acid. These decompositions are rationalized on the basis of expansion of the three-membered episulfone ring to a four-membered cyclic sulfinate or a five-membered dioxathiolane ring. The possible significance of ring expansion of episulfones to 1,3,2-dioxathiolanes in determining the observed stereochemistry of decomposition of certain episulfones is discussed.

Two isomeric episulfoxides and one episulfone previously were reported to be obtained by oxidation of *cis*-dibenzoylstilbene episulfide by hydrogen peroxide in acetic acid.[4] Oxidation of an episulfide to an episulfoxide or episulfone in an acidic medium is rare; only a patent claims such a synthesis.[5] Several examples of oxidation of episulfides to episulfoxides by sodium metaperiodate in aqueous methanol have been reported, but these episulfoxides are unstable in acid.[6] No other example of oxidation of an episulfide to an episulfone is known. The episulfide, episulfoxide, and episulfone of dibenzoylstilbene represent the first examples of episulfide derivatives in which the thiirane ring is substituted by electron-withdrawing carbonyl groups.

Results and Discussion

Heating the episulfone at about 300° (25 mm) gave benzil (34, 31%), diphenylacetylene (26, 31%), the lactone (**1**) of 4-hydroxy-2,2,3,4-tetraphenyl-3-butenoic acid (3, 7%), and unreacted episulfone. These products are unusual because episulfones usually lose sulfur dioxide readily and stereospecifically to yield an olefin which in the above case would be *cis*-dibenzoylstilbene. In fact,



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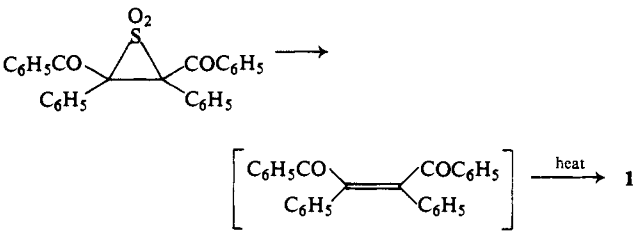
the lactone may be derived from *cis*-dibenzoylstilbene because pyrolysis of the latter at 270° has been reported to give the lactone quantitatively.[7]



Although the stereospecific decompositions of episulfones by loss of sulfur dioxide have been investigated extensively[8] and have been useful in the synthesis of

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(1) This work was aided by Grant GP-5513 of the National Science Foundation and Grant CA08250 of the National Cancer Institute of the National Institutes of Health.

(2) Reported in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts of Papers, P-19.

(3) For further details see G. E. Kuhlmann, Ph.D. Thesis, Syracuse University, 1968, and G. C. Levy, A.B. Honors Thesis, Syracuse University, 1965.

(4) D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30**, 636 (1965). Evidence has been obtained that the episulfide reported in this paper was *cis* (see ref 3).

(5) S. B. Soloway, U. S. Patent 2,694,073 (1954); *Chem. Abstr.*, **49**, 3465 (1955).

(6) G. E. Hartzell and J. N. Paige, *J. Am. Chem. Soc.*, **88**, 2616 (1966).

(7) D. R. Berger and R. K. Summerbell, *J. Org. Chem.*, **24**, 1881 (1959). However, when *trans*-dibenzoylstilbene is heated to its boiling point the lactone 1 is reported to be formed: N. Zinin, *Jahresber.*, 409 (1875). For definitions of the old terminology see F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **57**, 662 (1890). We have found that *trans*-dibenzoylstilbene is stable at least to 250°.

(8) (a) N. P. Neurelter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963); N. P. Neureiter, *ibid.*, **88**, 558 (1966); N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); (b) L. A. Paquette and L. S. Wittenbrook, *J. Am. Chem. Soc.*, **89**, 4483 (1967); (c) F. G. Bordwell and J. M. Williams, Jr., *ibid.*, **90**, 435 (1968).